In-situ Measurement of Growth Strains in Oxides

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SCIENTIFIC ACHIEVEMENT

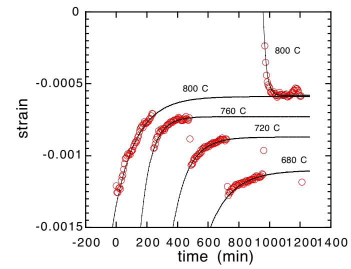
In situ x-ray measurements at the Advanced Photon Source have begun to reveal the behavior of growth strains in thermally grown protective oxides. We have monitored the temperature-dependent development of growth strains in chromium and aluminum oxides as the oxides nucleate and grow, and have monitored the response of the oxides to strain perturbations. For Cr_2O_3 grown on Fe-Cr-Ni alloys, we have demonstrated that new (lateral) growth occurs *within the existing oxide* to generate large compressive stresses. Growth does not occur exclusively at the oxide-atmosphere or oxide-metal interfaces, nor exclusively in grain boundaries parallel to the sample surface. The strain state depends on the interplay of compressive growth stresses that result from the internal deposition of new oxide, and plastic flow, which provides strain relief. For this study, we exploited the thermal expansion difference between the oxide and substrate to reduce the compressive strain to near zero (with an appropriate temperature adjustment). Remarkably, a rapid increase in the compressive stress occurs as oxidation continues. This re-establishment of a high compressive stress condition, countering effects of creep relaxation, must result from new growth occurring internal to the constrained oxide, providing confirmation of the Rhines-Wolf model of oxidation. For samples of β-NiAl, both pure and Zr-doped, and oxidized at 1100 C, we find that large *tensile stresses* appear in the oxide (Al_2O_3) in relatively early stages of α-Al_2O_3 formation. The early tensile strains, which decay with continued oxidation, are probably associated with the transformation of low density transition aluminas, which form below 1000 C, as they change to the stable α-phase.

SIGNIFICANCE

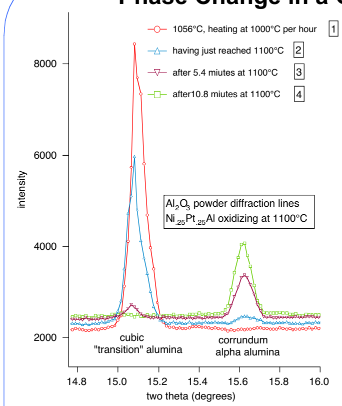
Insights obtained from this study may have positive impact on high temperature materials applications. For example, turbine blades for aircraft and land-based energy generation systems are protected from high temperature corrosive environments by a protective oxide coating that forms naturally at high temperatures. Improved engine performance and higher efficiency operation will depend on the development of improved protective oxide coatings. This undertaking will require a thorough understanding of the role of stresses (and resultant strains) that develop in protective oxides during operation. Planned measurements of strains under varying conditions of temperature, thermal cycling and environment will yield important insights into growth mechanisms and may lead to new methods for controlling the properties of the natural protective layer.

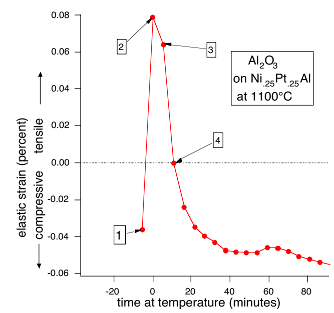
Response to Application and Removal of Stress

Compressive growth strain occurs in Cr_2O_3 formed on Fe-Cr-Ni alloy; the strain responds when a stress is imposed by changing the temperature. Note that when the temperature is changed from 680 to 800 °C, the strain is initially close to zero. Thereafter a compressive growth strain is quickly restored, apparently resulting from growth internal to the oxide. Solid lines are fits to a model which accounts for creep relaxation and compressive growth stress.



Phase Change in a Growing Oxide Stratum

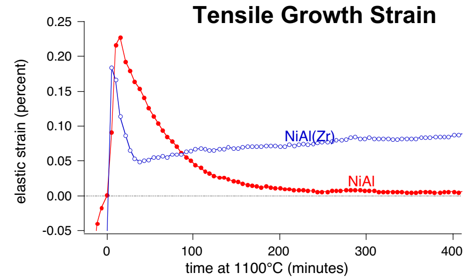




The evolving powder diffraction lines (shown on the left) of the Al_2O_3 growing on (and constrained by) Ni-Pt-Al alloy at 1100°C show that cubic "transition" Al_2O_3 is transforming into alpha Al_2O_3 , the high temperature stable phase. Corresponding to each diffraction pattern, 1 through 4, is an elastic strain (shown on the right) that is determined by analysis of each of the diffraction patterns on the left. It is seen that elastic strain becomes tensile while the transformation is proceeding and reverts to compressive after the transformation is complete. Such an evolution of strain is consistent with the fact that the density of alpha Al_2O_3 is considerably greater than the density of "transition" Al_2O_3.

Measurements of the growth strain exhibited by alpha alumina growing on single-crystal specimens of NiAl and NiAl(+0.06% Zr) yielded the results shown at right. The tensile strain associated with the transformation of cubic alumina to alpha alumina is not surprising, nor is the decay to near zero of the growth strain in the oxide on NiAl. However, the tensile growth strain (increasing with time) of alpha alumina on NiAl(Zr) is quite unexpected. Annihilation of cation and anion vacancies at grain boundaries has been suggested as a mechanism. The appearance of tensile growth strain in the protective oxide of an alloy which develops a very robust protective oxide, concurrent with the addition of a reactive element to that alloy, would seem to bear on understanding the reactive element effect.

Tensile Growth Strain



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